Indian J. Phys. 49, 603-614 (1975)

Some studies on the electrical properties of antimony films

D. C. Barua and K. Barua

Department of Physics, Dibrugarh University, Dibrugarh 786004

(*Received* 1 *March* 1975, *revised* 28 *April* 1975)

The electrical properties viz., resistivity, temperature coefficient of resistance (TCR) and Hall mobility μ_H of Sb films (100–6000 Å thick), deposited on optically flat glass slides at 25, 100 and 150°C have been studied. The presence of activation energy ΔE and negative TCR in room temperature deposited films of thickness 100–300 Å have been explained on the basis of *island structure theory* of Neugebauer (1964). The thickness dependence of the electrical properties are explained on the basis of classical size effect models for metals.

1. Introduction

The semimetallic element Sb has been a subject of study because of many interesting electrical properties. Electrical resistivity of thin Sb films was found to be same when measured by direct current and also at frequencies 0.92×10^{10} and 2.65×10^{10} c/sec (Clark 1955). Resistivity, Hall coefficient and magneto-resistance studies on thin Sb films ($<$ 900 Å) have established the existence of size effects (Colombani *et al* 1958). The transport properties and quantum oscillations in Sb films at low temperature have been observed by a number of authors (Grenier *et al* 1965, Komnik & Bukhshtab 1967, Brandt *et al* 1967, Komnik *et al* 1970, Bansal & Duggal 1972a, 1972b) and the amplitude of oscillation was found to decrease with increasing temperature.

This paper describes the results of measurements of the electrical properties viz., thickness dependence of resistivity, TCR, activation energy, Hall mobility, etc. of antimony films (100–6000 Å) at room temperature Films were deposited at 25, 100 and 150°C and the effect of deposition temperature was noted.

2. Experimental

2.1. *Film preparation.*—Antimony films were prepared by thermal evaporation of the metal (99.9%) from a nichrome wire basket in a vacuum $\simeq 10^{-5}$ torr. The substrates used were optically flat glass slides degassed at 300°C over two hours. Films were deposited at three different substrate temperatures viz., 25 (room temperature), 100 and 150°C. To prepare films of progressive thickness, under more or less similar deposition conditions, the source was positioned at

one end and at a distance $\simeq$ 10 cms below the array of the substrates. Normally 10 to 12 films were prepared at a time. The film geometry used for Hall measurements is shown in figure 1. (Goswami & Ojha 1973, Deokar & Goswami 1966). All the films were annealed in vacuum $\simeq 10^{-5}$ torr at 150°C for two hours unless otherwise stated.

2.2. *Film thickness measurements*—Film thicknesses were measured by multiple-beam interferometric method utilising Fizeau fringes of equal thickness. The strong green line of mercury (5461 Å) was used to produce the fringes.

2.3. *Measurements of electrical properties.*—For Hall measurements of uniform magnetic field of strength 4000 Gauss was produced by a 4 inch electromagnet. The field strength was measured ($\pm 2\%$ accuracy) using a Gaussmeter. The Hall voltage was measured with usual precautions using a vernier potentiometer (accuracy $\pm 0.1\ \mu$V) by changing the magnetic field and sample current directions. The sample current was measured from the voltage drop across a suitable resistance plugged out from the third arm of a P O. box in series with the film. The film resistance was measured from the voltage drop across the resistivity probes (probes 3 and 5 in figure 1) and from the knowledge of the current through the sample.

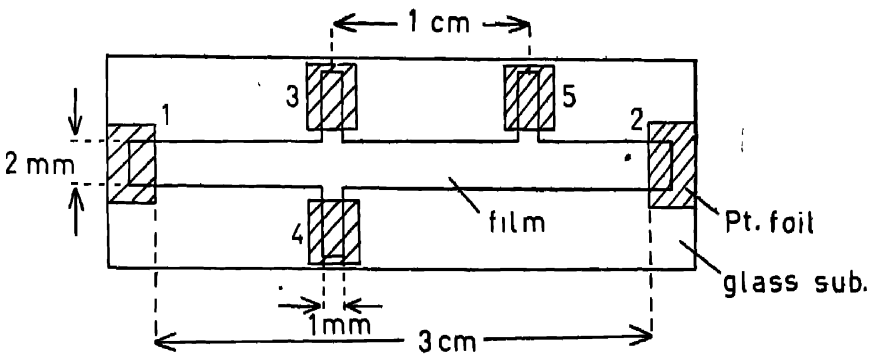

Fig. 1. Film geometry in Hall measurements.

The film temperature was measured (in case of temperature dependence of resistance measurements) using fine wire chromel-alumel thermocouple. Electrical contacts were established by pressing thin platinum foils against the Hall, resistivity and current probes. In some cases thick silver films were deposited over the Hall and resistivity probes and then the pressure contacts were made. Thin silver wires were used as conducting leads.

All the measurements were carried out in a vacuum of $\simeq 10^{-2}$ torr. The results reported here are for films aged in vacuum for few days.

3. Results

3.1. *Thickness dependence of resistivity*—Figure 2 is a plot of resistivity versus film thickness for 25, 100 and 150°C deposited films. In all the cases the resistivity was found to decrease very rapidly within the thickness range of 100 to 500 Å. The variation of resistivity was much smaller, but quite appreciable, in the thickness range 500 to 1000 Å. Above 1000 Å, however, very little variation of resistivity with thickness was observed.

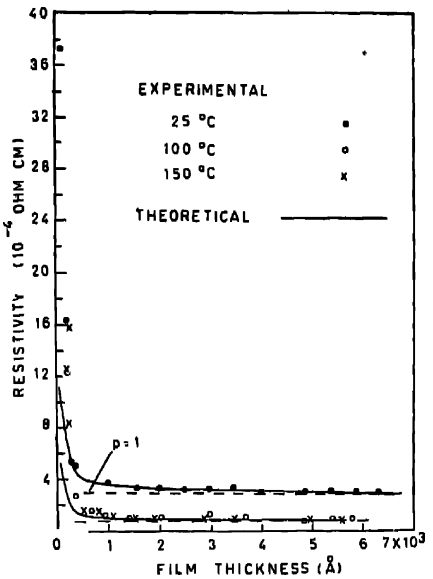

Fig. 2. Resistivity versus thickness; film deposited at 25, 100 and 150°C.

3.2. *Variation of resistance with temperature and TCR*—Temperature variation of resistance in Sb films deposited at 25°C was studied within the range −10 to 150°C. Resistance of the films within the thickness range 100 to 300 Å was found to decrease with the increase of temperature, whilst above 300 Å film thickness increase of resistivity with temperature was observed. TCR was calculated using relation

$$\text{TCR} = \frac{1}{\rho}\frac{d\rho}{dT} = \frac{1}{R}\frac{dR}{dT}$$

from resistivity versus temperature graphs near room temperature. Figure 3 is a plot of TCR versus film thickness. TCR was found to be fairly constant above 1000 Å, while below this, TCR decreased rapidly with the decrease of film thickness. Below 300 Å this parameter was found to be negative.

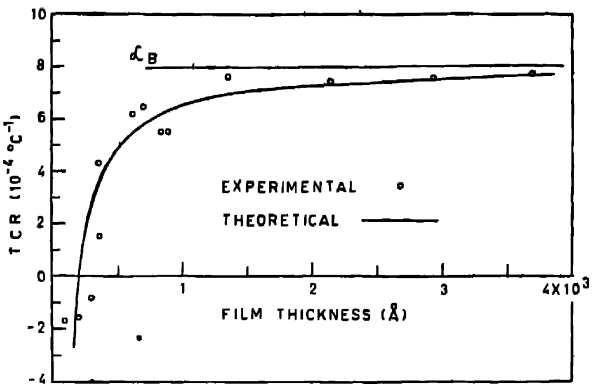

Fig. 3. TCR versus thickness; film deposited at 25°C.

Figure 4 shows log R versus $1/T$ curves for three typical antimony films (thickness $\leqslant$ 300 Å) deposited at 25°C. Activation energy was calculated by equating the slopes to $\Delta E/k$, k being the Boltzmann constant. Because of the two linear portions of the curves two ΔE values were obtained for the two temperature regions. ΔE was found to increase with the decrease of film thickness.

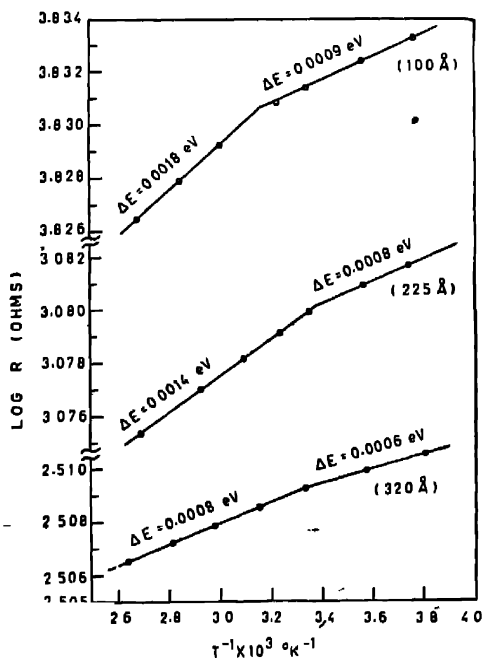

Fig. 4. log R versus $1/T$; film deposited at 25°C.

3.3. *Hall effect studies.*—All the films showed p-type conduction. This was ascertained from Hall measurements. The carrier concentration (h) was determined using free carrier relation $h = \frac{1}{|R_H|.e}$ and the Hall mobility was calculated from the relation $\mu_H = R_H.\sigma$, where σ is the measured conductivity. Table 1 shows the values of σ, R_H, μ_H and h for different films deposited at 25, 100 and 150°C.

Table 1. Variation of σ, R_H, μ_H and h with film thickness and substrate temperature.

Substrate temperature	d (Å)	σ ($10^3\Omega^{-1}cm^{-1}$)	R_H (cm^3/C)	μ_H (cm^2/V-sec)	h ($10^{20}cm^{-3}$)
	100	0.263	0.86	2.27	7.267
	200	0.555	1.62	8.98	3.858
	400	2.170	2.01	43.9	3.109
25°C	1150	4.758	1.67	79.0	3.742
	2200	6.097	1.65	101.0	3.788
	2750	6.173	1.63	102.0	3.834
	3700	6.329	1.68	106.0	3.720
	6250	6.412	1.70	109.0	3.676
	330	2.000	1.63	32.6	3.834
	800	8.695	1.72	149.3	3.634
	1400	9.350	1.60	148.3	3.900
	2050	9.700	1.78	173.3	3.511
100°C	3700	10.200	1.68	171.2	3.720
	4950	10.870	2.02	219.0	3.094
	5400	11.111	2.03	223.0	3.079
	5800	11.363	1.98	226.0	3.156
	550	3.750	1.72	64.7	3.634
	1500	9.970	1.71	170.4	3.655
	1800	10.420	1.74	181.3	3.592
150°C	3450	11.760	1.83	215.5	3.415
	4850	12.500	1.89	237.0	3.307
	5600	13.350	1.92	257.0	3.255

Figures 5 to 7 show the thickness dependence of μ_H in 25, 100 and 150°C deposited films. In all the cases μ_H was found to increase rapidly with thickness within the range 100–2500 Å. Above 4000 Å, however, μ_H remained independent of film thickness. In general μ_H increased with deposition temperature. For example, at 4000 Å the values of μ_H in 25, 100 and 150°C deposited films are 110, 210 and 230 cm^2/V-sec respectively. The effect of substrate temperature was, however, not so significant at lower thickness (< 500 Å).

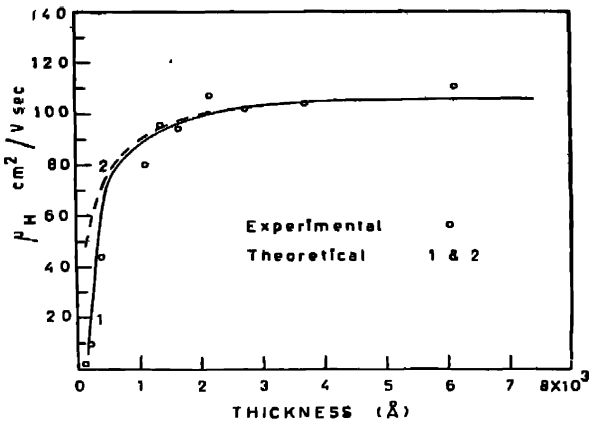

Fig. 5. μ_H versus thickness in 25°C deposited films.

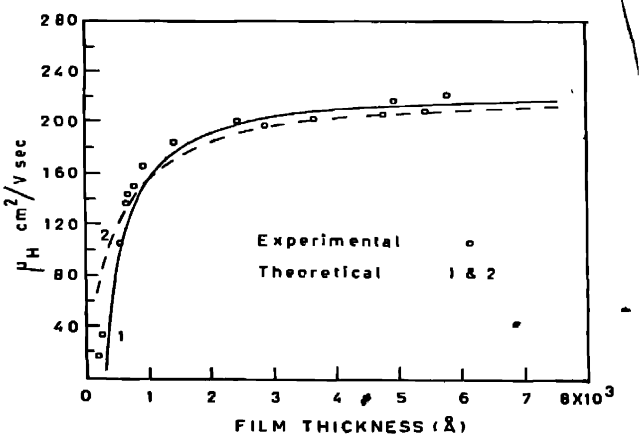

Fig. 6. μ_H versus thickness in 100°C deposited films.

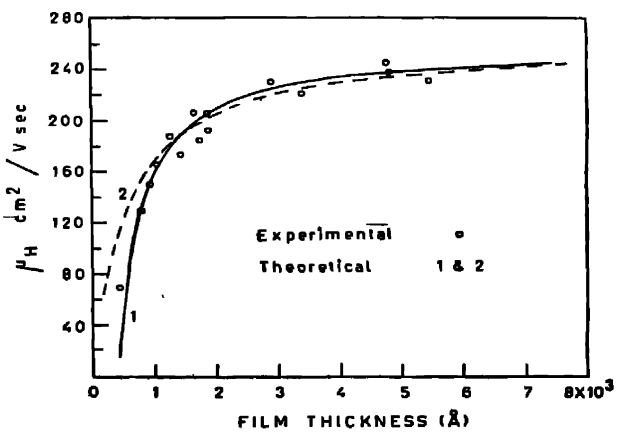

Fig. 7. μ_H versus thickness in 150°C deposited films.

4. Discussion

4.1. *Resistivity, TCR, etc.*—The thickness dependence of resistivity can be well understood in terms of the classical size effect model (Fuch 1938 ; Sondheimer 1952). This effect is essentially due to the reduction of the carrier mean free paths (mfp) caused by a scattering at the boundary of the thin film. The resistivity of a continuous, thin, plane, parallel, conducting film is

$$\rho_F = \rho_B \left[1+\frac{3}{8}\frac{l}{d}(1-p)\right], \tag{1}$$

where ρ_B is the resistivity of the bulk Sb with similar structure and same density of defects; p is the specularity parameter; l is the mfp of the carriers and d is the film thickness. For polycrystalline films, it is reasonable to assume that $p = 0$ (Chopra 1969) and eqn. (1) can be writtten as

$$\rho_F = \rho_B\left[1+\frac{3}{8}\frac{l_0}{d}\right], \tag{2}$$

where l_0 is the mfp for $p = 0$. Plotting $\rho_F.d$ as a function of d (figure 8) the values of ρ_B and l_0 can be determined from the intercept and slope of the straight

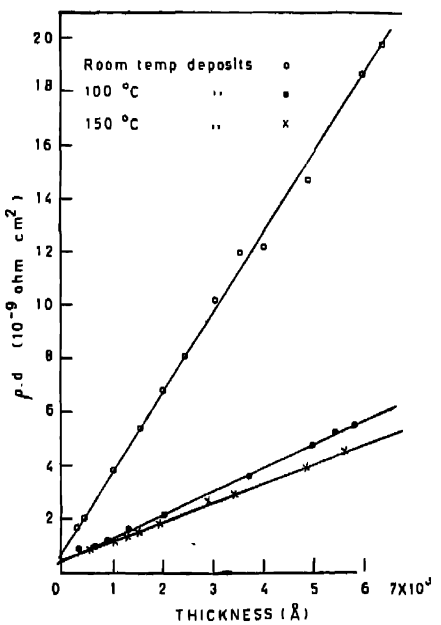

Fig. 8. ρ_F .d versus d curves.

lines. Table 2 shows these values. It is thus seen that with the increase of substrate temperature the bulk resistivity ρ_B decreases while the mfp of the carriers increases.

Table 2. ρ_B and l_0 values for 25 (room temperature), 100 and 150°C deposited films.

Deposition temperature	ρ_B (ohm-cm)	l_0(Å)
25°C	$3\ 060 \times 10^{-4}$	520
100°C	0.889×10^{-4}	900
150°C	0.755×10^{-4}	1130

The negative TCR, at the first sight, appears to be due to quantum size effect (QSE). The thickness at which QSE would appear is given by $d = \frac{n\hbar}{(2m^*\Delta)^{\frac{1}{2}}}$, where Δ is the band separation and other symbols have their usual meanings. For $\Delta = 0.03$ eV and taking $m^* = 0.5\, m_0$ for antimony, where m_0 is the rest mass of electron, $d \simeq 50$ Å. Again negative TCR is observed in island films. Since quantum oscillation was not observed in the present investigation, we suspected the films to be island structure films. To ascertain the cause of negative TCR the following simple experiment was performed.

Films of thickness 100 to 300 Å were deposited on room temperature substrates and annealed in vacuo successively at 65, 95, 125 and 150°C for three hours at each temperature The activation energy, after each annealing, was determined within the temperature range of −10 to 65°C from the measurements of resistance as a function of temperature (figure 9). It is seen that on annealing

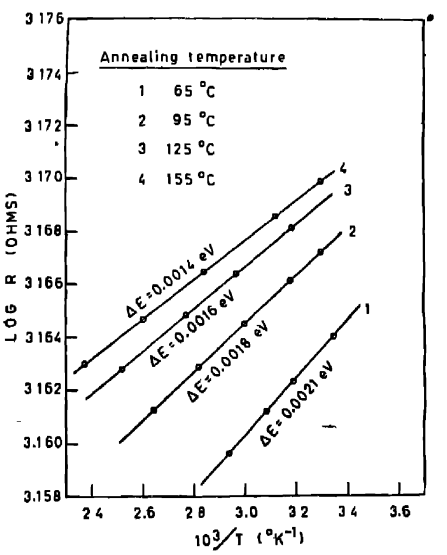

Fig. 9. Effect of successive annealing on room temperature deposited Sb films.

the film resistance increases whilst activation energy decreases. The increase of resistance on annealing appeared to be due to additional agglomeration of ultra thin films which, as deposited, was already discontinuous Similar behaviour was explained as due to the effect of heat treatment which caused the motion of the smaller islands leading to coalescence with larger ones (Skofronick & Phillips 1966).

According to Neugebauer (1964) an increased island size (r) would mean a reduction of activation energy when tunnelling mechanism of conduction prevails,

since ΔE where ϵ is the dielectric constant of the tunneling medium.

Thus lowering of ΔE with annealing temperature indicated that the films were indeed island type and the conduction mechanism appeared to follow the activated tunnelling process.

The presence of two activation energies in discontinuous Sb films can be explained on the assumption of two average island sizes. Hill (1969) classified discontinuous metal films according to island size, interisland spacing, predominant type of conduction mechanism and activation energy. Table 3 shows the classification. Two distinctly different regions of temperature-dependent conductivity in composite discontinuous films of gold-rich islands grown on palladium nuclei was also observed by Tick & Fehlner (1972), and the results have been explained on the basis of the existence of two average island sizes as observed by electron microscope. Since the mechanism of conduction in Sb ultra thin films is tunneling, our films may be classified as Hill Type I and III. However, the assumption of the presence of two average island sizes in Sb films deposited on glass could only be verified by electron microscopic observations which is beyond the scope of this laboratory.

The positive TCR was due to continuous nature of the films. The thickness dependence of TCR for thick film approximation ($d/l_0 >> 1$) is

$$\alpha_F = \alpha_B \left[1 - \frac{3}{8}\frac{l_0}{d}\right]. \qquad \ldots (3)$$

Taking $l_0 = 520$ Å, the value determined from resistivity size effect measurements, the best fit of the experimental data is obtained for $\alpha_B = 8 \times 10^{-4}\ °K^{-1}$. The theoretical curve and the experimental data are shown in figure 3.

4.2. *Hall effect studies.*—The thickness dependence of carrier mobility for thick film approximation ($d/l_0 >> 1$) is,

$$\mu_F = \mu_B \left[1 - \frac{3}{8}\frac{l_0}{d}\right]. \qquad (4)$$

Taking l_0 values from table 2 it is found that for the best fit of the experimental data μ_B should have values 110, 230 and 260 cm²/V-sec for 25, 100 and 150°C

deposited films respectively. The increase of carrier mobility with deposition temperature is quite expected since higher substrate temperatures favour the growth of bigger crystallites and such films are with lesser grain boundaries and stacking faults. However, in addition to these, concentration of frozen- in imperfections present in films increases with the decrease of deposition temperature. These would result in the increase of residual electrical resistivity (Mayadas & Rosenberg 1969, Mayadas *et al* 1969) and hence the decrease of carrier mobility of metal films. Fuchs theory is capable of explaining the thickness dependence of electrical properties arising out of the limitation of the carrier mfp by the geometrical boundary of the film. Deviations of the ρ_F, TCR and μ_F versus d curves from the experimental data below 1000 Å film thickness may be attributed to the appearance of voids and due to the scattering centres such as frozen-in imperfections which depend strongly on the deposition conditions and the thickness of the polycrystalline fims.

Table 3. Classification of type of films according to island size, interisland spacing and predominant type of conduction.

Type of film	Island size	Interisland spacing	Predominant type of conduction	Activation energy
I	small	small	activated tunneling	large
II	small	large	thermionic emission	small
III	large	small	activated tunneling	small
IV	large	large	thermionic emission	small
V	—	—	oxide-skin conduction	large

Many *et al* (1965) proposed a simpler theory according to which the unilateral mfp (l_u) is

$$l_u = \frac{\mu_B}{e}\left(\frac{m^* kT}{2\pi}\right)^{\frac{1}{2}}. \qquad \ldots (5)$$

and the effective mobility $< \mu_F >$ is

$$< \mu_F > = \mu_B \left[\frac{1}{1+2l_u/d}\right], \qquad \ldots (6)$$

From eq. (5) $< \mu_F >$ values are calculated using μ_B and m^* values (as already mentioned) for $T = 300$ °K. The values of l_u are 117.8, 245.7 and 277.8 Å for 25, 100 and 150°C deposited films respectively. With these values of l_u, $< \mu_F >$ values are calculated for different values of d using eq. (6). The agreement between the theoretical curves and experimental data are quite well above 1000 Å.

The carrier mfp can also be calculated from conductivity and Hall data using free carrier relation,

$$\sigma = \frac{he^2l}{m^*v}, \qquad \ldots (7)$$

where $h = \frac{8\pi}{3}\left(\frac{m^*v}{h}\right)^3$ is the carrier concentration; v is the velocity at the surface of Fermi distribution and the other symbols have their usual meanings. Thus the mfp is

$$l = 1.27 \times 10^4 \, h^{-2/3} \rho_B^{-1}. \qquad \ldots (8)$$

Taking $h = 3.67$, 3.1 and 3.25×10^{20} cm^{-3} as the bulk carrier concentrations of the film materials with same densities of defects as those of the films and ρ_B values from table 2, l values are estimated as 81, 312 and 356 Å for 25, 100 and 150°C deposited films respectively. It may be mentioned that $\rho_B l_0$ for vapour deposited metal films, other than monovalent and noble metarials, determined from size effect measurements, is always larger in comparison to the value determined from eq. (8) (Larson 1971). Again the assumptions of partial or total scattering in eq (1) would yield longer mfp's rather than decrease in values. Thus specular scattering need not be considered to eliminate the discrepancy between the values determined by the resistivity size effect measurements and conductivity and Hall data. It was proposed (Cotti *et al* 1964) that the mfp determined by a size effect measurement would allow primarily for those parts of the Fermi surface which have the longest mfp's.

5. Conclusions

The following conclusions are obtained from the study of electrical properties of Sb films :

1. Room temperature deposited Sb films on glass slides within the thickness range of 100–300 Å are discontinuous. The conduction process in these discontinuous films is activated tunnelling (Neugebauer 1964).

2. The thickness dependence of resistivity, TCR and Hall mobility at room temperature can be explained quantitatively with the help of classical size effect theory. The discrepancy in the lower thickness region ($d < 1000$ Å) is attributed to the appearance of voids, scattering of the carriers at the film surfaces and to the scattering by frozen- in structural imperfections.

3. The negative TCR in films within the thickness range of 300 to 100 Å was due to island structure of the films.

4. The increase of carrier mfp's, ρ_B and μ_B with deposition temperature are due to the rapid increase of grain size and removal of defects like stacking faults, grain boundaries, etc. by the thermal energy during deposition.

5. The presence of two activation energies in the two temperature regions was assumed to be due to two average island sizes.

References

Bansal S. K. & Duggal V. P. 1972 *Phys. Status Solidi B* (Germany) **55**, 407.

Bansal S. K. & Duggal V. P. 1972 *Nuclear Phys. Solid State Phys. Symp. Bombay*, p. 1.

Brandt N. B., Svistova E. A. & Gorskaya T. V. 1967 *Zh. Eksper. Teor. Fiz* (*USSR*) **53**, 1274.

Chopra K. L. 1969 *Thin Film Phenomena* Mc Graw-Hill New York Ch. VI.

Clark D. E. 1955 *Brit. J. Appl. Phys.* **6**, 158.

Colombani A , Vautier C & Huet P. 1958 *C.R. Acad. Sci.* (*Paris*) **247**, 1838.

Cotti P., Fryer E. M. & Olsen J. L. 1964 *Helv. Phys. Acta* **37**, 585.

Deokar V. D. & Goswami *A Proc Intern Symp. on Basic Problems in Thin Film Physics, Clausthal, Vandenhoek and Ruprecht* Gottingen, 1966, p 653.

Fuchs K. 1938 *Proc. Cambridge Phil. Soc.* **34**, 100.

Goswami A. & Ojha S. M. 1973 *Thin Solid Films* **16**, 187.

Grenier C. G , Long J. R., Reynolds J. M. & Zebouni N H. 1965 *Proc. 9th Inter. Conf. on Low Temp. Phys.* Columbus, New York, Plenum Press Pt. B p. 802.

Hill R. M. 1969 *Proc. Roy. Soc.* (*London*) **A309**, 377, **A309**, 397

Komnik Yu. F. & Bukhshtab E I. 1967 *JETP Letters* (*USA*) **2**, 58.

Kominik Yu. F., Bukhshtab E. I. & Nikitin Yu. V. 1970 *Fiz. Tverd. Tela* (*USSR*) **12**, 793.

Larson D. C. 1971 *Physics of Thin Films* Vol. 6, Ed. G. Hass & R. E. Thun p. 81.

Many A., Goldstein Y. & Grover N. B. 1965 *Semiconductor Surfaces* North Holland Publ. Co. Amsterdam p. 307.

Mayadas A. F , & Rosenberg J J. 1969 *J. Electrochem. Soc.* **116**, 1742.

Mayadas A. F., Shatzkes M. & Janak J. F. 1969 *Appl. Phys. Letters* **14**, 345.

Neugebauer C. A. 1964 *Physics of Thin Films* Vol. 2 Ed. G. Hass R. E. Thun. Academic Press, New York, London, p. 1.

Skofronick J. E. & Phillips W. B. 1966 *Proc. Int Symp.* Van der Hoeck and Ruprecht, Clausthal p. 591.

Sondheimer E. H. 1952 *Advan. Phys.* **1**, 1.

Tick P. A. & Fehlner F. P. 1972 *J. Appl. Phys.* **43**, 362.